IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of	**MAIL STOP RCE**
Yoichi Kodama et al.	Group Art Unit: 1711
Application No.: 10/671,565	Examiner: MELAINE D BISSETT
Filed: September 29, 2003	Confirmation No.: 4272
For: METAL LAMINATE	

DECLARATION UNDER 37 C.F.R. §1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Masao KAWAGUCHI, hereby declare as follows:

I have graduated from a Masters Course of Toyohashi Technology University in 2002 and been employed in Mitsui Chemicals, Inc. in April of 2002.

I was assigned immediately to the Electronic & Engineered Laboratories of Mitsui Chemicals, Inc. and have been engaged in the development of flexible circuit substrates since January 2003.

I have read and am familiar with the above-identified patent application and the references cited by the Examiner, i.e., U.S. Patent No. 4,987,207 to Yamaya et al. (hereinafter "Yamaya"), and U.S. Patent No. 5,508,357 to Matsuura et al. (hereinafter "Matsuura").

I carried out the following Experiments so that the present invention could be more fully understood by the Examiner.

REPORT OF EXPERIMENTS

1. Object of Experiments

The object of these experiments is to prove that using the bismaleimide compound linked at the meta-position (1,3-bis(3-maleimidephenoxy)benzene) that is specified in the present invention shows lower glass transition temperature and shows excellent peel strength when added to polyimide resin of the same type, in comparison with using the bismaleimide compound linked at the para position (1,3-bis(4-maleimidephenoxy)benzene) and other bismaleimide compounds disclosed by the Yamaya (bis(4-maleimidephenoxy)methane).

2. Method and Results of the Experiments

I conducted the reproduction test according to Example 1 of the present patent application and a similar experiment to Example 1 on two kinds of bismaleimide compounds which fall outside the scope of Claim 1 to confirm adhesion.

Synthesis 1: Synthesis of 1,3-bis(3-maleimidephenoxy)benzene (APB-BMI)

23.4 g of p-toluenesulfonic acid monohydrate (produced by Wako Pure Chemical Industries Ltd), 13.4 g of N, N-dimethylaniline (produced by Wako Pure Chemical Industries Ltd) and 732 g of toluene (produced by Wako Pure Chemical Industries Ltd) were charged to a reactor with an agitator, a reflux tube with a Dean-Stark trap and a nitrogen-introducing tube. The temperature was raised to the reflux temperature (110ºC) in an atmosphere of nitrogen, and the water distilled was separated and removed by the Dean-Stark trap.

After confirming that the distillation of water has ceased, 366 g of toluene (produced by Wako Pure Chemical Industries Ltd) were added to 233.9 g of 1,3-bis(3-aminophenoxy)benzene (hereinafter called "APB" in some cases) (produced by Mitsui Chemicals, Inc.) containing 180.4 g of maleic anhydride (produced by Wako Pure Chemical Industries Ltd) and were dissolved by heating.

As a result, a toluene solution of APB was obtained (concentration: 39 wt%). This toluene solution of APB was put in a jacketed dropping funnel and dropped and charged to the reactor in 13 hours. During the dropping, the inside of the reactor was kept in a state of toluene being refluxed at all times, and the water distilled was separated and removed by the Dean-Stark trap consecutively.

After the contents were further aged for 2 hours, cooled to 70ºC, and washed six times with 300 g of hot water (70ºC). The organic layer after the washing was cooled to room temperature, and the deposited crystals were filtered, washed with toluene and dried at 60ºC under vacuum.

As a result, 307.6 g of 1,3-bis(3-maleimidephenoxy)benzene were obtained. (Purity of APB-BMI as determined by HPLC: 97.1%)

Further, analysis was conducted by high-performance liquid chromatography (hereinafter referred to as "HPLC").

Analytical conditions are as follows:

- Column: YMC-Pack ODS-A A-312 6.0 ϕ mm x 150 mm (of YMC)
- Column temp.: 40ºC
- Detection wavelength: 270 nm

- Eluent: Acetone/water/85% phosphoric acid
  = 620/380/0.05 (vol/vol/vol)
- Flow rate: 0.9 ml/min

Experiment 1: Reproduction of Example 1

12.00 g of 1,3-bis(3-aminophenoxy)benzene (produced by Mitsui Chemicals, Inc.), 15.94 g of 1,3-bis(3-maleimidephenoxy)benzene produced as described in Synthesis 1 above and 48.70 g of N, N-dimethylacetoamide (produced by Junsei Chemical Co. Ltd.) were put into a container with an agitator and a nitrogen-introducing tube, and agitated for 1 hour at 50ºC in an atmosphere of nitrogen.

After that, the temperature in the system was reduced to 20ºC, 11.90 g of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) (produced by Daicel Chemical Industries Ltd.) were added in installments with care being taken of a rise in the solution temperature, heated to 50ºC again, and agitated for 4 hours.

After part of the solution thus obtained was taken and cast onto a glass plate, it was heated at a temperature rise rate of 7ºC/minute from 50ºC to 270ºC. As a result, film 20 μm in thickness was obtained. The glass transition temperature (Tg) of the resultant polyimide film was measured by use of a differential scanning calorimeter (available from Mac Science Co., DSC3110) at a temperature rise rate of 10ºC/minute. The glass transition temperature (Tg) was 106ºC.

A part of the resultant polyamic acid solution containing bismaleimide compound was cast onto copper foil (available from Nippon Denkai Ltd., SLP-35, 35 μm thick) and heated from 50ºC to 270ºC at a temperature rise rate of 7ºC/minute. As a result, a metal laminate with 12 μm polyimide layer thickness was obtained.

In order to evaluate the adhesion of the laminate, the laminate was heat-bonded to copper foil (available from Nippon Denkai Ltd., SLP-35, 35 μm thick) at 190ºC and 3 MPa for 2 seconds by means of a pulse bonder (available from Kel Company Ltd., TC-1320UD). 90º peeling test was conducted on the test specimen in accordance with IPC-TM-650 method 2.4.9. As a result, the peel strength was 1.4 kN/m.

Synthesis 2: Synthesis of 1,3-bis(4-maleimidephenoxy)benzene (APB-R-BMI)

5.87 g of p-toluenesulfonic acid monohydrate (produced by Wako Pure Chemical Industries Ltd), 3.34 g of N, N-dimethylaniline (produced by Wako Pure Chemical Industries Ltd) and 183 g of toluene (produced by Wako Pure Chemical Industries Ltd) were charged to a reactor with an agitator, a reflux tube with Dean-Stark trap and a nitrogen-introducing tube. The temperature was raised to the reflux temperature (110ºC) in an atmosphere of nitrogen, and the water distilled was separated and removed by the Dean-Stark trap.

After confirming that the distillation of water has ceased, 91.5 g of toluene (produced by Wako Pure Chemical Industries Ltd) were added to 58.5 g of 1,3-bis(4-aminophenoxy)benzene (hereinafter called "APB-R" in some cases) (produced by Mitsui Chemicals, Inc.) containing 45.1 g of maleic anhydride (produced by Wako Pure Chemical Industries Ltd) and were dissolved by heating.

As a result, a toluene solution of APB-R was obtained (concentration: 39 wt%). This toluene solution of APB-R was put in a jacketed dropping funnel and dropped and charged to the reactor in 9 hours. During the dropping, the inside of the reactor was kept in a state of toluene being refluxed at all times, and the water distilled was separated and removed by the Dean-Stark trap consecutively.

After the contents were further aged for 2 hours, cooled to 70ºC, and washed six times with 75 g of hot water (70ºC). The organic layer after the washing was cooled to room temperature, and the deposited crystals were filtered, washed with toluene and dried at 60ºC under vacuum.

As a result, 71.9 g of 1,3-bis(4-maleimidephenoxy)benzene (APB-R-BMI) were obtained. (Purity of APB-R-BMI as determined by HPLC: 97.0% (by the same measuring method as for APB-BMI))

Experiment 2:

12.00 g of 1,3-bis(3-aminophenoxy)benzene (produced by Mitsui Chemicals, Inc.), 15.94 g of 1,3-bis(4-maleimidephenoxyn)benzene produced as described in Synthesis 2 above and 48.70 g of N, N-dimethylacetoamide (produced by Junsei Chemical Co. Ltd.) were put into a container with an agitator and a nitrogen-introducing tube, and agitated for 1 hour at 50ºC in an atmosphere of nitrogen. After that, the temperature in the system was reduced to 20ºC, 11.90 g of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) (produced by Daicel Chemical Industries Ltd.) were added in installments with care being taken of a rise in the solution temperature, heated to 50ºC again, and agitated for 4 hours.

After part of the solution thus obtained was taken and cast onto a glass plate, it was heated at a temperature rise rate of 7ºC/minute from 50ºC to 270ºC. As a result, film 20 μm in thickness was obtained. The glass transition temperature (Tg) of the resultant polyimide film was measured by use of a differential scanning calorimeter (available from Mac Science Co., DSC3110) at a temperature rise rate of 10ºC/minute. The glass transition temperature (Tg) was 115ºC.

A part of the resultant polyamic acid solution containing bismaleimide compound was cast onto copper foil (available from Nippon Denkai Ltd., SLP-35, 35 μm thick) and heated from 50ºC to 270ºC at a temperature rise rate of 7ºC/minute. As a result, a metal laminate with 12 μm polyimide layer thickness was obtained.

In order to evaluate the adhesion of the laminate, the laminate was heat-bonded to copper foil (available from Nippon Denkai Ltd., SLP-35, 35 μm thick) at 190ºC and 3 MPa and for 2 seconds by means of a pulse bonder (available from Kel Company Ltd., TC-1320UD). 90º peeling test was conducted on the test specimen in accordance with IPC-TM-650 method 2.4.9. As a result, the peel strength was 1.0 kN/m.

Experiment 3:

12.00 g of 1,3-bis(3-aminophenoxy)benzene (produced by Mitsui Chemicals, Inc.), 15.94 g of bis(4-maleimidephenoxy)methane produced (hereinafter referred to as "BMI-S" in some cases) (produced by KI Chemical Co., registered trademark: BMI) and 48.70 g of N, N-dimethylacetoamide (produced by Junsei Chemical Co. Ltd.) were put into a container with an agitator and a nitrogen-introducing tube, and agitated for 1 hour at 50ºC in an atmosphere of nitrogen. After

that, the temperature in the system was reduced to 20ºC, 11.90 g of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) (produced by Daicel Chemical Industries Ltd.) were added in installments with care being taken of a rise in the solution temperature, heated to 50ºC again, and agitated for 4 hours.

After part of the solution thus obtained was taken and cast onto a glass plate, it was heated at a temperature rise rate of 7ºC/minute from 50ºC to 270ºC. As a result, film 20 μm in thickness was obtained. The glass transition temperature (Tg) of the resultant polyimide film was measured by use of a differential scanning calorimeter (available from Mac Science Co., DSC3110) at a temperature rise rate of 10ºC/minute. The glass transition temperature (Tg) was 120ºC.

Moreover, part of the resultant polyamic acid solution containing bismaleimide compound was cast onto copper foil (available from Nippon Denkai Ltd., SLP-35, 35 μm thick) and heated from 50ºC to 270ºC at a temperature rise rate of 7ºC/minute. As a result, a metal laminate with 12 μm polyimide layer thickness was obtained.

In order to evaluate the adhesion of the laminate, the laminate was heat-bonded to copper foil (available from Nippon Denkai Ltd., SLP-35, 35 μm thick) at 190ºC and 3 MPa for 2 seconds by means of a pulse bonder (available from Kel Company Ltd., TC-1320UD). 90º peeling test was conducted on the test specimen in accordance with IPC-TM-650 method 2.4.9. As a result, the peel strength was 0.7 kN/m.

The glass transition temperature (Tg) and peel strength as determined by the above experiments are shown in the table below.

Table 1

	Diamine compound	Dianhydride	Bismaleimide compound	Tg (DSC method)	Peel strength
	mol	mol	wt%	°C	kN/m
Example 1	APB 0.041	BTDA 0.0369	APB-BMI 40	106	1.6
Experiment 1	APB 0.041	BTDA 0.0369	APB-BMI 40	106	1.4
Experiment 2	APB 0.041	BTDA 0.0369	APB-R-BMI 40	115	1.0
Experiment 3	APB 0.041	BTDA 0.0369	BMI-S	120	0.7

3. Consideration of the Experiments:

As the result of the experiments, it is understood that the using bismaleimide compound linked at the meta-position that is specified in the present invention shows lower in glass transition temperature and higher peel strength than other bismaleimide compounds and therefore is useful for use in metal laminates.

That the undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief to be true, and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

Date: 15/03/2006 By: Masao Kawaguchi